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Evaluation of the atmospheric pollution by pesticides using lichens as biomonitors

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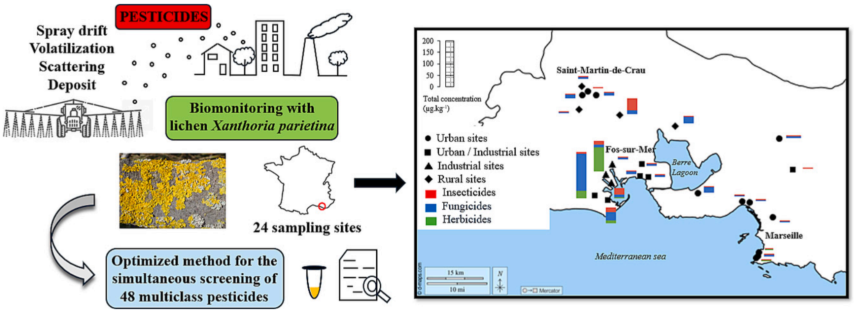
HIGHLIGHTS

- Lichens can be used to monitor the atmospheric exposure to pesticides.
- Reliable method for simultaneous screening of 48 pesticides was developed.
- 15 pesticides, including 4 banned, detected in all 24 sites of southern France.
- 13 detected pesticides considered as priority active substances in air monitoring.
- Lichen biomonitoring revealed possibly high contamination of industrial areas.

GRAPHICAL ABSTRACT



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ABSTRACT

The extensive use of pesticides combined with their persistence in the environment requires new methodologies to assess more effectively the population exposure to pesticides via air pollution. Biomonitoring pesticides with lichens has been poorly documented, although it represents a complementary approach to the usual active samplings, with an exposure to pesticides accumulated and integrated over several months. An optimized extraction procedure from the lichen *Xanthoria parietina* followed by a gas chromatographic-tandem mass spectrometric analysis is proposed here to quantify simultaneously 48 pesticides considered in France as priority active substances to monitor in the air. This method has been applied to lichen samples collected in 24 sites in southern France covering urban, industrial, and agricultural areas in order to identify potential contrasts related to anthropogenic activities. Fifteen pesticides (six fungicides, five insecticides, and four herbicides), including four active compounds currently banned by EU legislation, were detected in at least one site. Lindane, diflufenican, difenoconazole, and boscalid were the most common pesticides found in all sites. Urban sites appeared generally less contaminated compared to industrial and rural ones, but a strong heterogeneity was noticed between locations. The biomonitoring with lichens revealed unexpected contaminated areas, partly due to the use of herbicides for vegetation control in industrial and railway installations. The spatial distribution also suggests an input of pesticides by atmospheric transport at the local and regional scales.

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1. Introduction

In 2022, according to the most recent statistics on agriculture, forestry, and fisheries in the European Union (UE), the total quantity of pesticide sales amounted to 322,000 tons with a major use of fungicides (43 %) and herbicides (35 %). Contrary to the general decline of pesticide sales observed in the UE between 2011 and 2022, France saw an increase in active ingredient use in the same period and registered the highest volume sold in 2022 (67,800 tons), making it the largest consumer of pesticides among EU member states (Eurostat, 2024). Despite their benefits for crop yield, the intensive and widespread use of pesticides raises concerns due to the contamination of natural resources and their possible effects on human health (Damalas and Eleftherohorinos, 2011). Chronic exposure to pesticides is considered as a risk factor for developing diseases such as non-Hodgkin lymphoma, multiple myeloma, prostate cancer, Parkinson's disease, cognitive disorders and respiratory impairments (Inserm, 2022). Depending on their application, only a minor fraction of the applied pesticides reaches their targets (Pimentel and Burgess, 2012; Zivan et al., 2017), while the remaining ends up on soil, surface waters or in the atmosphere and is thereafter dispersed through several processes including volatilization, wind erosion, leaching or runoff (Fenner et al., 2013). Studies have shown that pesticide drift may account for a few percent to 25 % of pesticide loss during spraying in agricultural areas (Tudi et al., 2021). In addition, volatilization may represent a major pathway of mass transfer from soil or plants to the atmosphere, accounting for 2 to 90 % of the applied dose (Bedos et al., 2002). Although there is currently no regulation controlling pesticides in the atmosphere, their monitoring appears necessary to provide a greater knowledge about their occurrence in the environment, to understand their fate and partitioning and characterize organism exposure levels. To this purpose, an interesting tool is offered by using lichens as biomonitors (Abas, 2021; Blett et al., 2003). Lichens are organisms resulting from a symbiotic association of a fungus and a chlorophyll-containing partner, either algae or cyanobacteria (Nash, 2008). Lichens receive all their nutrients and water from wet and dry atmospheric deposition, which makes them very sensitive to air pollution and thus valuable as air quality indicators (Conti and Cecchetti, 2001; Nimis et al., 2002; Ratier et al., 2018). Their wide geographical distribution and abundance allow studies over a large area with a low-cost sampling procedure and minimal materials required. Lichens accumulate pollutants in their pseudo-tissues during at least several months or years of exposure (Dron et al., 2021; Loppi and Paoli, 2015) constituting a complementary approach to the usual methods favoring active sampling of air over a period of a few dozen hours (Yusà et al., 2009).

The determination of various pollutants in lichen pseudo-tissues can yield valuable information about their occurrence in the environment. Many studies have already been conducted to monitor metals with lichen pseudo-tissues (Garty, 2001; Nimis et al., 2001; Parzych et al., 2016; Ratier et al., 2018). For organic compounds, biomonitoring studies using lichens are scarce and mainly focus on polycyclic aromatic hydrocarbons, (Augusto et al., 2010; Dron et al., 2021; Ratier et al., 2018; Studabaker et al., 2017; Van der Wat and Forbes, 2019), polychlorinated biphenyls (Herzig et al., 2019; Ratier et al., 2018), dioxins and furans (Augusto et al., 2007, 2016; Ratier et al., 2018) and markers of biomass burning (Dauphin et al., 2020). Regarding pesticides, to our knowledge the few studies reported mainly focused on organochlorine pesticides (Herzig et al., 2019; Schrlau et al., 2011; Villeneuve et al., 1988; Zhu et al., 2015) and glyphosate (Lucadamo et al., 2018; Vannini et al., 2016). The determination of pesticides in lichens is technically challenging because concentrations are expected to be low and natural substances, *eg.* issued from lichen pseudo-tissues, can interfere with the targeted compounds during the spectrometric analyses. An optimized method for the simultaneous screening of 48 pesticides, mostly currently used or recently banned substances, in lichen samples is proposed here. This method was validated and subsequently applied to real lichen samples collected in 24 sites across the Aix-Marseille-Provence metropolitan area (south of France), characterized by the presence of numerous and diversified anthropogenic activities. The objectives of this study were to (1) investigate the occurrence of pesticides in the atmosphere in this area using lichen biomonitoring, (2) evaluate if lichens are relevant to biomonitor pesticides in contrasted environments influenced by various anthropic activities.

2. Materials and methods

2.1. Study area

Sampling sites were located in southern France, between the Rhône delta and the Marseille urban area. This region, Aix-Marseille-Provence metropolitan area, is one of the most densely populated in France, hosting around 2 million people (INSEE, 2021). The high density of industries, maritime activities, human infrastructures, and agricultural activities make this territory prone to high pollution levels. Agricultural areas cover 26 % of the territory, with an activity mainly oriented towards arboriculture, market gardening, and viticulture. Sites were specifically chosen for their different context of human activities in order to form a representative panel of exposure to pesticides in the study area. To establish this selection, the area was meticulously characterized in terms of land use and anthropic activities based on the national databases available on polluted sites and soils, pollutant emissions, pesticide sales, and cadastral data (Austruy, A., 2022). Sites were categorized as urban, industrial or rural areas based on the surrounding dominant land use. Marseille (pop. 873,076) and Aix-en-Provence (pop. 147,478) are the two largest cities of the area (INSEE, 2021). Gardanne (pop. 21,124) and Châteauneuf-les-Martigues (pop. 17,909) are part of the Aix-en-Provence – Marseille urban agglomeration and are close to vegetable and cereal crops. Fos-sur-Mer (pop. 15,469) is the main maritime industrial zone in France including a vast petrochemical complex, various industries (steel, energy, chemistry, urban and industrial waste incineration units) and world-leading maritime terminals (containers, ore, oil, gas, cereal). Port-Saint-Louis-du-Rhône is also an industrial town (pop. 8,446) with important maritime and petrochemical activities. It is also known for its many marshes and an agricultural production towards rice farming and cereals. Saint-Martin-de-Crau (pop. 13,729) is a rural town with wide natural areas with more than 17,000 ha of protected steppes dedicated to the cultivation of “Crau hay” (Registered Designation of Origin) and orchards. It also has surfaces allocated to market gardening and the production of olives, nuts, and cereals. Finally, Cornillon-Confoux (pop. 1,571) is a rural town with nearly 55 % of its land dedicated to agricultural activities, mainly the cultivation of vegetables, fruits, viticulture, and field crops. A total of 24 sampling sites including 11 urban sites, 6 urban/industrial sites, 3 industrial sites and 4 rural sites were selected and are presented in detail in Table 1. Highly populated areas were prioritized, as shown by the selection of a majority of urban sites, due to the sanitary concerns surrounding pesticide use.

The climate is Mediterranean with mild winters and warm, dry summers. According to data from the meteorological station of Marseille-Marignane (Météo-France, 2021) during the six months preceding the sampling, the mean temperature was 20.6 °C with 1,774 h of sunshine and a total of 234 mm rainfall. Northwesterly winds dominate in this region (approx. 40 %), but winds from the southeast and the east may also contribute up to 25 % in summer when sea-breeze conditions are frequently observed (Ratier et al., 2018; Dron et al., 2021).

2.2. Field samplings

Lichen samples were collected from October 4 to 15, 2021. For consistency and to allow comparison between sites, collection was performed during the shortest possible period so that sampling was representative of homogeneous environmental conditions. It has been shown that the bioaccumulation of very different contaminants such as

Table 1

Exact locations of the 24 sampling sites (WGS84 coordinates), their type (U: Urban; UI: Urban/Industrial; I: Industrial; R: Rural;) and their characteristics.

Site Name	Location	Latitude (°N)	Longitude (°E)	Type	Description
AIX	Aix-en-Provence	43.519823	5.449357	U	Urban park
CHF	Châteauneuf-les-Martigues	43.390106	5.156074	U	Urban area near market gardening
MN1	Marseille (north)	43.363657	5.327305	U	Urban park, near railroad
MN2	Marseille (north)	43.365753	5.309998	U	Urban park close to the coast
MRS	Marseille (center)	43.326250	5.400930	U	Urban park
MS1	Marseille (south)	43.239063	5.367627	U	Urban park near the Calanques National Park
MS2	Marseille (south)	43.229105	5.354494	U	Natural area in the Calanques National Park
MS3	Marseille (south)	43.231481	5.360910	U	Urban residential area near the Calanques National Park
SME	Saint-Martin-de-Crau	43.636588	4.827686	U	Urban park near major road
SMN	Saint-Martin-de-Crau	43.643431	4.808055	U	Urban residential area near organic cereal farming
SMO	Saint-Martin-de-Crau	43.635539	4.791997	U	Urban park near golf course
ENG	Fos-sur-Mer	43.431389	4.974244	UI	Urban residential area near ponds and chemical industry
FOA	Fos-sur-Mer	43.433084	4.947911	UI	Urban park near ponds and major road
FOM	Fos-sur-Mer	46.463835	4.947756	UI	Urban park near industrial area
GAR	Gardanne	43.454223	5.465259	UI	Urban area near chemical industry
PSL-S3	Port-Saint-Louis-du-Rhône	43.396682	4.803336	UI	Urban park near market gardening
PSL-S10	Port-Saint-Louis-du-Rhône	43.386845	4.850011	UI	Coastal area
CAB	Fos-sur-Mer	43.439625	4.839973	I	Natural area near chemical, energy industries and railway
GOU	Fos-sur-Mer	43.417650	4.860107	I	Natural area near chemical industries and incinerator
TON	Fos-sur-Mer	43.459677	4.851368	I	Natural area near energy companies and chemical industries
COR	Cornillon-Confoux	43.566907	5.070480	R	Park near sport field
CPH	Saint-Martin-de-Crau	43.654700	4.790452	R	Park near Crau hay prairies
ENT	Saint-Martin-de-Crau	43.599995	4.896676	R	Natural area near orchads
TNT	Saint-Martin-de-Crau	43.612968	4.785948	R	Natural area near Crau hay prairies and pasture

PAHs and metals in the lichen *Xanthoria parietina* is representative of the atmospheric exposure over several months to 1 year, possibly more according to the exposure and climatic conditions (Augusto et al., 2009; Dron et al., 2021; Paoli et al., 2018; Zhao et al., 2019). Regarding the sampling period, and assuming that the studied pesticides show a comparable integration time, this integration time would cover spring and summer, when pesticides are predominantly applied. *X. parietina* is a ubiquitous and pollution-tolerant lichen specie, which can be found in rural, urban, and industrial areas. It is the most widely used lichen species in European bioaccumulation programs (Nimis et al., 2001) and the most represented in the study territory (Austruy, 2022). On each sampling site, *X. parietina* full thalli (> 3 cm diameter) were collected on at least 5 trees at a height of 1.2 to 2.5 m to minimize the influence of soil resuspension. The trees were selected at least 100 m away from potentially strong emission sources (high-traffic roads, cultivated fields, industrial installations, etc.), to ensure an exposure to diffuse atmospheric pollution and that lichens were in sufficiently good conditions. Visual control was also realized to discard necrotic lichen thalli from sampling. The lichen thalli were pulled off the tree bark using ceramic knives and stored away from light at 4 °C until preparation, which was done within 24 h. After removing unwanted materials (remaining bark, other lichen species, dust…), they were freeze-dried and finely ground in a ball mill equipped with ZrO_2 beads and capsules. The samples (approximately 1 g) were then stored at −45 °C until analysis.

2.3. Pesticides selection

The selection of pesticides was based on monitoring conducted by the Observatory for Pesticide Residues in the region Provence-Alpes-Côte-d'Azur region, France (ORP PACA) between 2012 and 2017 (Désert et al., 2018). Pesticides were chosen according to their regional sales quantity, their toxicity, their occurrence in the atmosphere and their suitability to the analytical method. A total of 48 active substances were chosen including 20 herbicides, 17 fungicides and 11 insecticides among which is an insecticide synergist (Table S1). The French Agency for Food, Environmental and Occupational Health & Safety (ANSES) classified 34 of these substances as priority active molecules to monitor in ambient air in France (Hulin et al., 2021). Among them, some are banned for years (e.g. lindane was prohibited in France for agricultural uses in 1998) but regarding their persistence in the environment, they can still be found in quantifiable concentrations (Désert et al., 2018).

2.4. Chemicals

Pesticide standards (purity >95 %) were purchased from Sigma-Aldrich (PESTANAL, analytical standard). Triphenyl phosphate (TPP; purity >99 %) was used as an internal standard and was purchased also from Sigma-Aldrich. A stock solution of each pesticide was prepared by dissolving the pure standard in dichloromethane (DCM) or acetonitrile (ACN). Standard mixed solutions were then prepared by diluting the stock solutions with ACN. Both the stock and working solutions were stored at −18 °C. All solvents used were of analytical grade and obtained from Sigma-Aldrich.

2.5. Chemical extraction and cleanup optimization

Accelerated Solvent Extraction (ASE 350, Dionex) was carried out to extract pesticides from the lichen samples. Approximately 0.5 g of lichen powder was precisely weighted and spiked with 20 μL of a 5 $mg.L^{-1}$ TPP solution before being introduced into the middle of a 66 mL stainless-steel cell filled with glass beads (VWR). Glass fiber filters (Thermo Scientific) covered both the top and the bottom of the cell. Two solvents were tested for the extraction, DCM and ACN, chosen for their ability to dissolve pesticides. The other extracting conditions were: temperature, 100 °C; pressure, 100 bars; heat up time, 5 min; static time, 5 min; flush volume, 70 % of the extraction cell volume; purge time, 300 s. Four

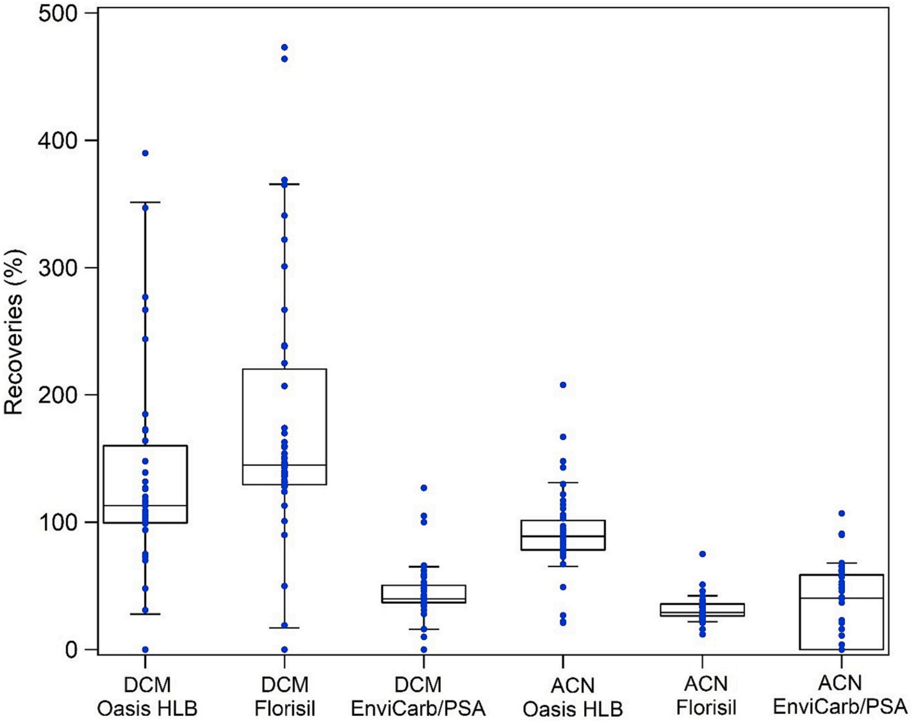

Fig. 1. Recoveries (%) comparison between different combinations of extraction solvents and clean-up sorbents on a lichen matrix spiked with pesticides. Each experiment was conducted in 3 replicates. Each point represents the average of the 3 replicates for each individual pesticide. At this stage, concentrations were not corrected by the internal standard. DCM: dichloromethane, ACN: acetonitrile.

cycles per cell were carried out to maximize the extraction recoveries. Extracts were reduced under a nitrogen stream at 40 °C (TurboVap II, Biotage) until reaching a volume of 5 mL. They were then purified using a Solid Phase Extraction (SPE) cartridge. The efficiency of three solid phases was compared: Florisil 500 mg (Sigma-Aldrich), Oasis HLB 150 mg (Waters) and Supelclean ENVI-Carb II 500 mg/PSA 300 mg (Sigma-Aldrich). The cartridge sorbent was initially conditioned with 6 mL of the extraction solvent (DCM or ACN). The extract was then slowly loaded and recovered in a clean vial after passing through the solid phase. The cartridge was rinsed with 6 mL of the extraction solvent, which was also recovered and added to the purified extract. The sample was then concentrated under a gentle N_2 stream at 40 °C to a volume of 500 μL, and finally filtered through a 0.45 μm PTFE syringe filter (Sigma-Aldrich). The extracts were conserved at −18 °C until analysis.

2.6. Sample analysis by gas chromatography – Mass spectrometry tandem (GC–MS/MS)

Sample analyses were performed with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ Quantum Triple Quadrupole (Thermo Scientific) operated in the electron impact ionization mode (70 eV). Most of the conditions were derived from a previous work carried out on atmospheric samples (Désert et al., 2018): column, TG-5MS (30 m*0.25 mm*0.25 μm, Thermo Scientific); carrier gas, helium at a constant flow rate of 1 mL.min^{-1}; splitless injector, splitless time of 2 min with surge pressure of 300 kPa during 2 min; injection volume, 1 μL; inlet temperature, 250 °C; transfer line temperature, 250 °C; oven temperature program, hold 2 min at 35 °C, then increased to 180 °C at a rate of 25 °C.min^{-1}, and finally increased to 300 °C at 5 °C.min^{-1}, which was held for 3 min. The ion source temperature was fixed at 250 °C. The MS was operated in multi reaction monitoring mode (MRM) using argon as collision gas at 1 mTorr. Transitions used to identify and quantify each pesticide are given in Table S2. Peaks were positively identified in correspondence with the retention time of the standard compound and considering that the intensity ratios of MRM transitions matched with those of the standards (Fig.S1).

2.7. Method validation

The recoveries of individual pesticides were determined by spiking known amounts of pesticides (0.25 μg) into a dry and ground lichen sample (0.5 g). Additionally, the linearity of the method was assessed by spiking a lichen matrix with known increasing quantities of pesticides (0.01; 0.02; 0.1; 0.25; 0.375 μg). Repeatability of the method was evaluated by determining the relative standard deviations (RSD) from 12 spiked replicates in lichen from 3 different sampling sites. The limits of detection (LODs) and quantification (LOQs) were calculated using the signal-to-noise ratio approach. Lichen matrix was spiked with known low concentrations of pesticides and the minimum concentration at which analytes could be reliably detected and quantified (signal-to-noise ratio of 3:1 and 9:1 respectively) were determined. As there is no commercially available certified pesticide-free lichen material, lichen used as a matrix was collected from an area with a low expected exposure to pesticides and was initially analyzed without additional substances to determine the initial pesticide content. The pesticides were either undetectable or found in negligible concentrations compared to the spiked quantities. The final method was then applied to a certified reference material (CRM) of wheat flour (ERM-BC706, European Commission's Joint Research Centre). This CRM was certified for the content of 7 pesticides targeted in this study in a vegetable matrix and was the most suitable reference material commercially available to assess the accuracy of the method.

3. Results and discussion

3.1. Method development

The selection of an appropriate extraction solvent plays a decisive role in achieving optimal extraction recoveries of pesticides. ACN and DCM were chosen for their efficiency in extracting a wide range of polar

Table 2

Results obtained for the validation of the analytical method (recovery, reproducibility, linearity, limits of detection and quantification), and for the analysis of the CRM ERM-BC706 (mean of 4 replicates). The results of these experiments include internal standard (TPP, triphenyl phosphate) correction.

Pesticide	Recoveries	RSD	Linearity R^2	LOD	LOQ	CRM conc calculated	CRM conc certified
	%	%	–	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}	µg.kg^{-1}
Aclonifen	103	30	0.999	31	93		
Chlorpropham	114	18	0.995	16	48		
Clomazone	94	15	0.990	0.3	0.9		
Diclofop-methyl	82	12	0.993	8	24		
Diflufenican	92	13	0.994	0.2	0.5		
Dimethenamid-P	92	16	0.992	0.3	0.9		
Flazasulfuron	91	11	0.972	3	9		
Flumioxazin	163	50	0.993	0.3	0.9		
Flurochloridone	85	13	0.992	16	48		
Isoproturon	64	15	0.977	1.6	4.8		
Lenacil	106	21	0.993	31	93		
Linuron	76	17	0.987	16	48	0.52 ± 0.07	0.51 ± 0.06
Metazachlor	87	14	0.994	1.6	4.8		
Oxadiazon	88	14	0.992	31	93		
Pendimethalin	101	18	0.993	2	6		
Propyzamide	89	17	0.993	3.1	9.3		
Prosulfocarb	89	14	0.982	8	24		
S-metolachlor	94	13	0.994	2	6		
Terbuthylazine	99	22	0.983	1.6	4.8		
Triallate	87	16	0.988	16	48		
Boscalid	113	34	0.991	0.3	0.9		
Cyprodinil	88	15	0.991	3	9		
Difenoconazole	166	48	0.988	0.3	0.9		
Dimethomorph	163	40	0.987	1.6	4.7		
Epoxiconazole	85	17	0.990	8	23		
Fenhexamid	136	29	0.994	1.6	4.8		
Fenpropimorph	82	16	0.991	1.6	4.8		
Fluazinam	42	14	0.981	160	500		
Flusilazole	94	22	0.997	16	48		
Folpet	29	9	0.997	160	500		
Iprodione	101	24	0.992	3	9		
Kresoxym-methyl	100	13	0.991	31	93		
Pyrimethanil	93	11	0.999	3	9		
Spiroxamine	97	27	0.992	16	48		
Tebuconazole	98	14	0.994	2	6	0.035 ± 0.008	0.041 ± 0.006
Tetraconazole	90	16	0.986	0.3	0.9		
Tolylfluanid	38	22	0.983	160	500		
Chlorpyrifos	91	14	0.995	0.3	0.9	2.42 ± 0.50	2.43 ± 0.23
Chlorpyrifos-methyl	91	12	0.995	16	48		
Cypermethrin	108	15	0.989	0.3	0.9	4.9 ± 0.7	3.7 ± 0.5
Deltamethrin	115	30	0.988	2	6	4.0 ± 0.6	3.8 ± 0.7
Fenoxycarb	95	15	0.996	16	48		
Fipronil	84	11	0.993	1.6	4.8	0.42 ± 0.05	0.42 ± 0.04
Lambda-cyhalothrin	92	20	0.990	16	48		
Lindane	83	13	0.987	0.3	0.9		
Permethrin	100	21	0.993	31	93	0.48 ± 0.06	0.40 ± 0.07
Piperonyl butoxide	107	20	0.995	31	93		
Pirimicarb	89	16	0.993	8	24		

and nonpolar compounds. Considering the high organic matter content in lichen samples, a clean-up step was deemed necessary and the Oasis HLB, Florisil, and EnviCarb/PSA sorbents were tested. Extraction with DCM led to co-extracted matrix components which were not efficiently removed during the clean-up step either with the Oasis HLB or the Florisil sorbents. The enhancement of the chromatographic signal due to the matrix effects resulted in excessively high recoveries above 130 % for 14 and 36 pesticides (among the 48 targeted) using the Oasis HLB and Florisil cartridges, respectively (Fig. 1). The matrix-induced signal enhancement is frequently observed during pesticides analysis of samples containing complex matrix components (e.g. lipids, pigments, resins, sugars, etc.) (Erney et al., 1993; Poole, 2007). The injection port of the GC is composed of active sites which are mainly free silanol groups present in the glass liner. The accumulation of non-volatile components originating from repeated analyses of samples may also result in the formation of active sites in the injector or in the first centimeters of the GC column. When the analytes prepared in pure solvent are injected, they may bind to these active sites, resulting in their incomplete transfer to the detector. However, when the same amount of analytes in a real sample is injected, the matrix components, typically the most abundant components of the sample in trace analysis, compete with the analytes to react with the active sites hence reducing losses during the injection. Therefore, overestimated concentrations may be achieved. Polar pesticides and pesticides with high molecular masses (> 400 g.mol^{-1}) are more likely affected by matrix effect (Sánchez-Brunete et al., 2005). Jiménez et al. (1998) reported recovery percentages >1000 % for certain pesticides such as parathion and folpet in honey matrices.

The EnviCarb/PSA sorbent appeared to be the most effective in removing matrix components, in particular chlorophyll compounds, sugars, and fatty acids but a significant fraction of the pesticides was also retained on the sorbent and was not eluted with either of the solvents tested. More than half of the molecules showed recoveries below 60 % (Fig. 1). Extractions performed with ACN followed by a clean-up step using an Oasis HLB cartridge provided satisfactory recoveries within 70–130 % for 39 pesticides (Table 2). Fluazinam, folpet and tolylfluanid showed poor recoveries at the concentration tested (around 23 %), but the spiked concentration was below the limit of quantification of the GC–MS/MS for folpet which may explain this result for this compound.

Table 3
Summary of results from reported studies using lichens as biomonitors of pesticides in the atmosphere.

Location	Sampling date	Lichen species	Pesticides	Extraction method	Clean-up step	Analysis method	Recovery	LOD	Mean concentration detected	Reference
Southern France	May 1986	*Usnea barbata*	11 organochlorine pesticides including lindane	Soxhlet extraction hexane	Florisil	GC-Electron Capture Detector (ECD)	Not reported	Not reported	Site1: 130 μg.kg^{-1} Site 2: 24 μg.kg^{-1}	Villeneuve et al. (1988)
United States - National parks	Summer 2004	*Letharia vulpina* *Xanthoparmelia* *Alectoria sarmentosa* *Platismatia glauca* *Masonhalea richardsonii*	65 semi-volatile organic compounds including lindane, chlorpyrifos, triallate and S-metolachlor	ASE extraction DCM	Water extraction and silica SPE	GC–MS	68 % (mean)	0.1658 μg.kg^{-1} (lindane) 0.3208 μg.kg^{-1} (triallate) 0.2521 μg.kg^{-1} (chlorpyriphos)	1.74–10.06 μg.kg^{-1} (lindane) 1.71–2.25 μg.kg^{-1} (chlorpyrifos)	Schrlau et al. (2011)
China -Tibetan Plateau	June 2010 and 2011	*Usnea longissima*	28 organochlorine pesticides including lindane	ASE extraction hexane/acetone (3:1)	Silicagel/alumina and C18 SPE	GC–MS	73 % (mean)	0.57–17 ng.kg^{-1}	0.15–1.3 μg.kg^{-1} (lindane)	Zhu et al. (2015)
Switzerland	1995 and 2014	*Parmelia sulcata*	30 organochlorine pesticides including lindane	Soxhlet extraction hexane/acetone (2:1)	Aluminum oxide and florisil	GC-High Resolution Mass Spectrometry (GC/HRMS)	39 % (13C lindane)	0.0625 μg.kg^{-1} (lindane)	12.74 μg.kg^{-1} in 1995 0.95 μg.kg^{-1} in 2014 (lindane)	Herzig et al. (2019)
Southern France	October 2021	*Xanthoria parietina*	48 pesticides (20 herbicides, 17 fungicides, 11 insecticides including lindane)	ASE extraction ACN	Oasis HLB	GC–MS/MS	90 % (mean) 83 % (lindane)	0.3 μg.kg^{-1} (lindane) 160 μg.kg^{-1} (highest value)	1.9 μg.kg^{-1} (lindane) 1.4 μg.kg^{-1} (chlorpyrifos)	This study

Finally, the Florisil clean-up of ACN extracts gave lower recoveries (31 % in average) than the Oasis HLB (90 % on average). According to these results, ACN was selected for its high ability to extract the pesticides while minimizing the amount of coextracted undesirable compounds and the Oasis HLB was shown to offer the best performances in terms of clean-up efficiency (Table S3).

3.2. *Method validation*

The accuracy of the method was evaluated using the certified reference material ERM-BC706, which includes certified concentrations for cypermethrin, deltamethrin, fipronil, linuron, permethrin, tebuconazole, and chlorpyrifos. Good agreement with the certified values was found for all compounds using the developed method, which is demonstrated by the measurement deviations, all included within the certified measurement uncertainty intervals. All pesticides exhibited good linearities in the studied range with regression coefficients higher than 0.99 for most of the compounds analyzed (Table 2). The reproducibility of the method was satisfactory, considering the nature of the analyzed matrix, with RSD $<$ 30 % for 45 out of 48 compounds. Higher RSDs were found only for the three pesticides that presented recovery rates around 160 %. It can be assumed that these compounds were subjected to matrix effects inducing higher variations in the chromatographic peak areas. Finally, the LOQ values ranged from 0.6 μg.kg^{-1} (diflufenican) to 500 μg.kg^{-1} for fluazinam, folpet and tolylfluanid for which lower recoveries were previously identified (Table 2). The validated method proposed here demonstrates significant improvements in recovery rates compared to previous studies (Table 3). The discrepancies observed for the detection limits may be attributed to variations in detector sensitivity and differences in the calculation methods used, which were not detailed in the previous studies. Although there is a consensus in the definition of the LOD, there is not an agreement in the way to calculate this parameter. For instance, the determination of the LOD considering the matrix may increase the values by several orders of magnitude compared to those obtained with standards solutions.

3.3. *Occurrence of pesticides in field samples*

The lichens collected in the 24 sites were analyzed in accordance with the previously developed method. Concentrations in lichen samples were adjusted for recoveries during the data treatment and are summarized in Fig. 2. All results are presented in detail in Tables S4-S7.

Out of the 48 pesticides analyzed, 15 were detected in at least one site. Among them, 13 pesticides are considered priority substances to monitor in the ambient air, and 4 pesticides are currently banned by EU legislation. Fungicides were the most frequently measured, showing a detection rate of 18 %, followed by insecticides (13 %) and herbicides (6 %). Individual pesticide concentrations ranged from 0.5 μg.kg^{-1} to 79.4 μg.kg^{-1}, with the maximum concentration observed for difenoconazole. Lindane, diflufenican, difenoconazole and boscalid were the most ubiquitous pesticides as they were detected in all sites. Despite its ban in 1998 and 2007 for agricultural and biocidal uses, respectively, lindane was found in 100 % of the lichen samples due to its persistence in the environment. This result supported the lindane analyses carried out between 2012 and 2017 in the Provence-Alpes-Côte-d'Azur Region, which showed a detection frequency of 99 % in the ambient air on daily filter samples (Désert et al., 2018). Therefore, it is consistent to find lindane in lichens where the accumulation takes place over several months. Lindane was relatively homogeneously distributed among locations (quantified concentrations ranging from 1.1 to 4.5 μg.kg^{-1}), which is also consistent with a regional-scale distribution, associated with ancient dispersion without recent use. Difenoconazole is a fungicide widely used for disease control in many fruits, vegetables, cereals, and various other grain crops. Its broad range of applications combined

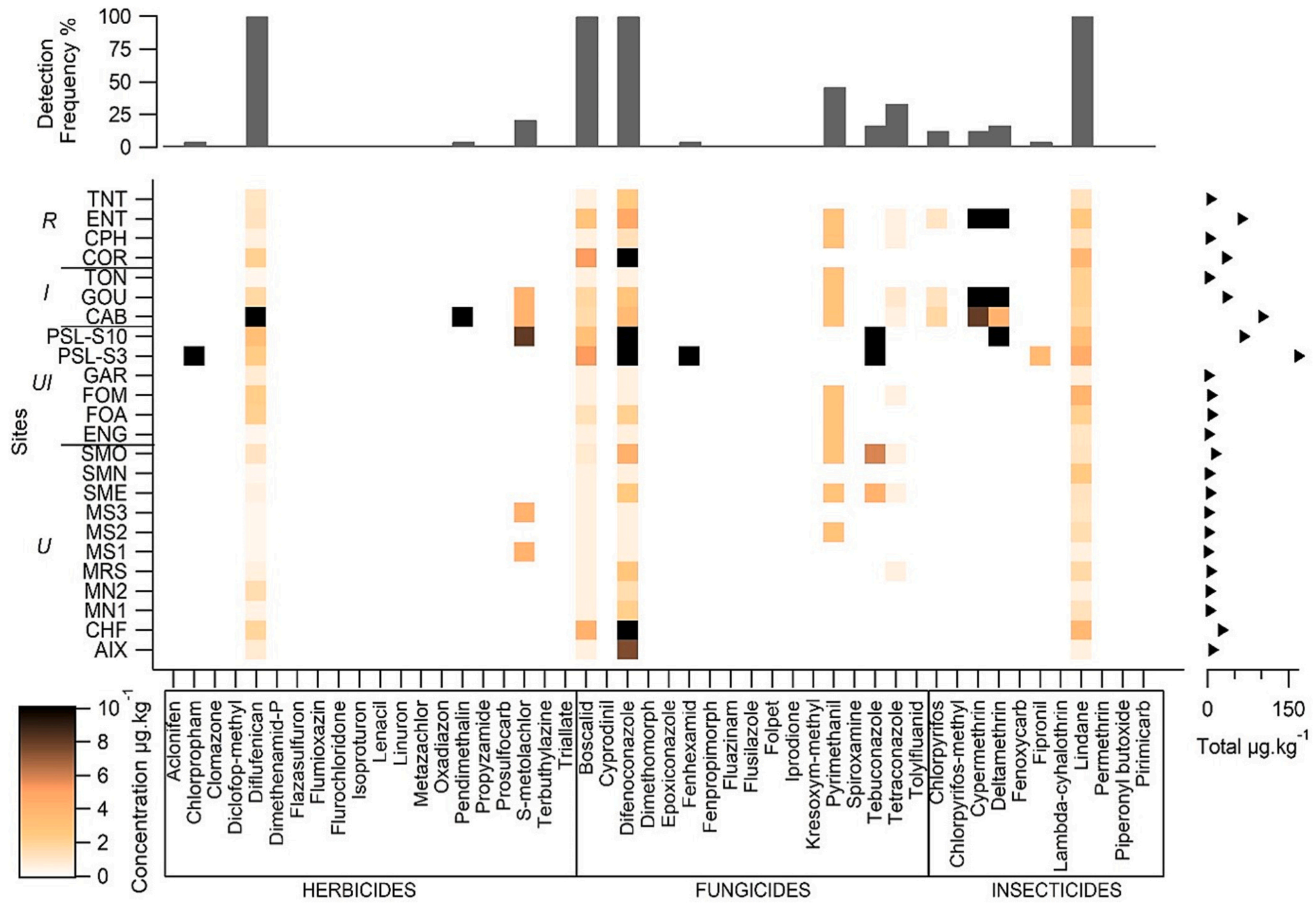

Fig. 2. Abundance of 48 pesticides in lichens sampled on the 24 sites. Each row represents a site and each column, a pesticide. Pesticides are ordered by pesticide class, i.e., herbicides, fungicides, and insecticides. The color range represents the level of the detected concentrations (black cells = concentration > 10 µg.kg^{-1}), whereas empty (white) cells indicate no detection (<LOD). For the pesticides detected but in concentrations under the LOQ, an arbitrary intermediate concentration equal to 2xLOD was assigned. The sum of the concentrations of quantified pesticides (>LOQ) for each site is given on the right. The bars at the top show the frequency of occurrence of each specific compound across all samples.

to its long atmospheric lifetime (Socorro et al., 2016) might explain the high detection rate and concentration levels. Boscalid is an efficient broad-spectrum carboximide fungicide applied to control plant pathogens during the production of numerous crops and fruits, especially in greenhouses. For its part, diflufenican is one of the most used herbicides with multipurpose applications, including urban weed control. Different studies reported the frequent detection of these pesticides in air samples in France and their potential for atmospheric transport which might explain their presence at all the sampling sites (Désert et al., 2018; Mayer et al., 2024; Schummer et al., 2010).

In addition to lindane, three more recently banned pesticides were sporadically detected. It concerns chlorpyrifos, chlorpropham and fipronil. The last two were detected only in one site (PSL—S3, Table S5). This result highlights the fact that the monitoring of banned pesticides should not be overlooked as they can still be employed for domestic uses (i.e. fipronil is allowed for parasite control on pets) or to get rid of old inventory. Significant amounts of the pyrethroids cypermethrin and deltamethrin, the herbicide s-metolachlor and the fungicide tebuconazole were found in several sites whereas the presence of pendimethalin and fenhexamid was clearly identified in one site for each substance. Finally, pyrimethanil and tetraconazole were detected but under the limits of quantification in various sites. All these compounds were also frequently quantified during the study made in this area from 2012 to 2017 (Désert et al., 2018), which confirms a preferential use of these pesticides at the regional scale.

The studies available in the literature that investigated the use of lichens for pesticide monitoring in the atmosphere are scarce and mainly limited to ancient organochlorine pesticides. The average concentrations for lindane and chlorpyrifos reported in the most recent studies ranged from 0.15 µg.kg^{-1} to 10.06 µg.kg^{-1} for lindane and from 1.71 to 2.25 µg.kg^{-1} for chlorpyrifos, levels that are similar to the values found in this work (1.9 µg.kg^{-1} and 1.4 µg.kg^{-1} in average for lindane and chlorpyriphos, respectively) (Table 3). Earlier studies provided historical data on the biomonitoring of lindane in the atmosphere, with concentrations reaching 130 µg.kg^{-1} when the use of lindane was still authorized, and thereafter a decrease was observed over time to get to the current levels (Table 3). Considering that these studies were conducted with different lichen species, in different regions, at different times, and without harmonized sampling and analytical protocols, any interpretation must be made with caution. However, these results still highlight the relevance of lichen biomonitoring for pesticides and the need to extend these measurements to other sites with the development of standardized protocols to facilitate the comparison of results between studies.

3.4. *Influence of anthropogenic activities*

The total pesticide concentrations exhibited strong differences between locations. Six sites showed higher concentrations compared to the others: PSL-S3 and PSL-S10 (Port-Saint-Louis-du-Rhône), CAB and GOU (Fos-Sur-Mer), ENT (Saint-Martin-de-Crau) and COR (Cornillon-Confoux) with concentrations reaching 168.4 µg.kg^{-1} in total for PSL—S3.

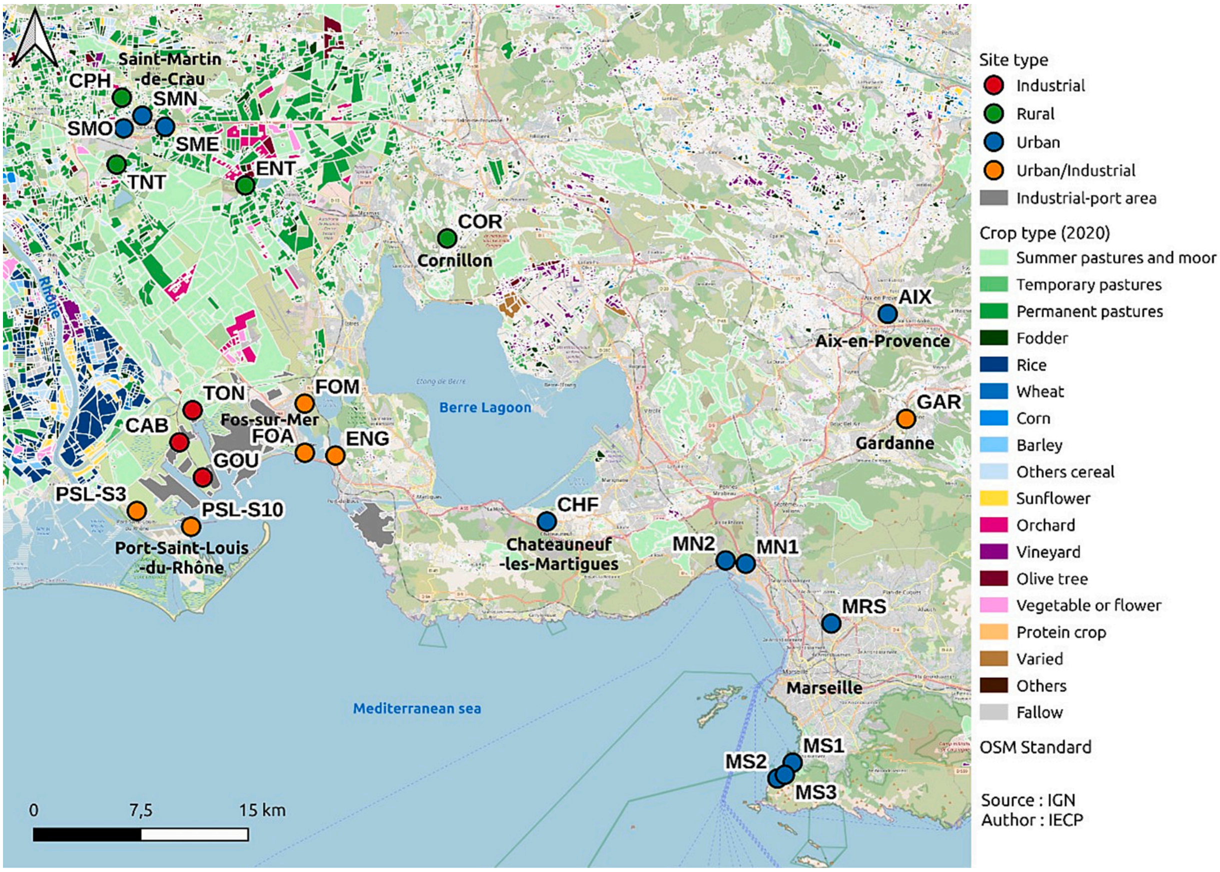

Fig. 3. Crop-type map of the study area. The sampling sites are identified by colored circles according to their typology.

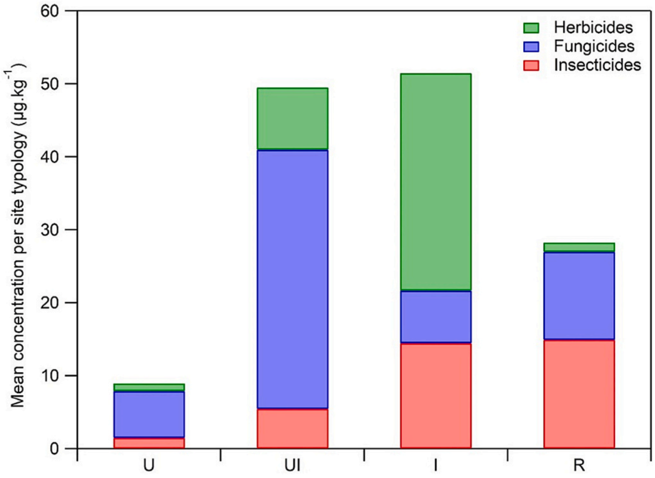

Fig. 4. Distribution of pesticides families i.e. herbicides, fungicides, and insecticides (mean concentrations in lichen) between urban (U), urban/industrial (UI), industrial (I), and rural (R) sites.

Conversely, the lowest total concentrations were found in the South Marseille sites (MS1, MS2, MS3) and Gardanne (GAR) with a total mean concentration of 0.9 $\mu g.kg^{-1}$. These high-concentration sites also exhibited the largest number of pesticides detected with 11 and 10 pesticides detected in the CAB and GOU sites respectively. The lichen sampled in the rural site ENT which is located near large orchards, olive trees, and greenhouse vegetable crops (Fig. 3) was characterized by high levels of insecticides (deltamethrin and cypermethrin) widely used in these crop types. Insecticides were also well detected on the west side of the industrial zone, in the sites GOU, PSL—S10, CAB, and PSL—S3, which are all downwind from large agricultural spaces (rice, vineyards, sunflowers, etc.) and possibly impacted by the mosquito control programs in the Camargue and Rhône delta wetlands located on the west side of the study area. Conversely, insecticide levels remained low in urban areas (Fig. 4).

Lichen samples collected in the industrial site CAB, and to a lesser extent, in PSL-S10 and PSL—S3, also had high levels of herbicides. Considering that around industrial installations, roadsides, railway tracks, etc., the aim of herbicides is the absolute destruction of all vegetation that might cause damage, present fire hazards, or impede work crews, these areas may reveal unconsidered hotspots. One such hotspot was identified here in the CAB site, with significantly higher concentrations of diflufenican (64.8 $\mu g.kg^{-1}$) and pendimethalin (19.6 $\mu g.kg^{-1}$) compared to other sites (not detected to 3.3 $\mu g.kg^{-1}$) (Tables S4-S7). Its proximity to a chemical plant and a railway terminal suggests intensive use of herbicides for weed control, including diflufenican, active substance used by the French national railroad company (SNCF). This is particularly concerning as wide-spectrum cocktail effects may arise from numerous chemical contaminants also present in this area (Ratier et al., 2018).

Fungicides were particularly concentrated in the Port-Saint-Louis-du-Rhône samples (PSL-S3 and PSL—S10), with higher concentrations of tebuconazole, difenoconazole, and fenhexamid measured compared to the other sites. The presence of tebuconazole and difenoconazole may result from their use in rice farming which is widely practiced in the Rhône Delta wetlands located northwest of the sampling sites that can consequently be impacted under northwesterly wind conditions (Fig. 3). Additionally, it is worth noting the proximity of cereal and peat terminals with open-air conditioning near these sites which could lead to atmospheric inputs of pesticides from stored cereals and peats. Finally, urban areas showed lower exposure to pesticides in the ambient air compared to rural and industrial areas, as revealed by integrative lichen biomonitoring, with average concentration levels 3 to 5 times lower than those in rural and industrial sites (Fig. 4).

4. Conclusions

The analytical method presented in this paper enabled the simultaneous analysis of 48 pesticides, mostly currently used or recently banned substances, in the lichen *X. parietina*. The combination of an ASE extraction method with acetonitrile followed by a purification step on an Oasis HLB sorbent allowed an efficient analysis by GC–MS/MS, demonstrated by satisfying recovery rates (ranging from 70 % to 130 %) for 81 % of the targeted pesticides. The validation of the method yielded positive results, indicating good performance in terms of linearity, accuracy, and precision. The analysis of lichen samples collected among 24 sites in various environments enabled the detection of 15 pesticides, including 6 fungicides, 5 insecticides, and 4 herbicides. Lindane, diflufenican, difenoconazole, and boscalid were the most detected at all sites, suggesting possible atmospheric transports at local and regional scales and persistence of these compounds in the atmosphere. The long-term integration achieved with lichen biomonitoring compared to instrumental techniques (filter sampling or on-line measurements) have revealed particularly valuable information concerning the distribution of pesticides according to anthropogenic activities, highlighting poorly documented and unexpected aspects such as the possibly high contamination sources in industrial areas or by transportation infrastructure. A complementary study, including a greater number of sites with similar profiles (crop type, road or rail infrastructures, industrial activity) and a better balance in the number of sites per typology, could be conducted to perform robust statistical analyses, which were not feasible here due to the heterogeneity and specificity of the selected sites. The experimental approach described in this work could be applied to other monitoring campaigns to map the spatial distribution of pesticides useful to identified contaminated areas and aid human health risk assessment studies. The determination of pesticides in lichens also illustrates their uptake by living species, and this monitoring methodology may be extended to other organic contaminants, thus providing information on potential cocktail effects.

CRediT authorship contribution statement

Amandine Durand: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Julien Dron:** Writing – review & editing, Conceptualization. **Pascale Prudent:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Henri Wortham:** Writing – review & editing, Supervision, Conceptualization. **Caroline Dalquier:** Investigation. **Mathilde Reuillard:** Visualization. **Annabelle Austruy:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177286.

Data availability

Data will be made available on request.

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Supplementary information:

EVALUATION OF THE ATMOSPHERIC POLLUTION BY PESTICIDES USING LICHENS AS BIOMONITORS

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Table S1. List of the studied pesticides, their CAS number, chemical substance family and, their status regarding European Union (EU) regulation. Priority substances have been highlighted.

Pesticide	**CAS number**	**Chemical class**	**Use[a]**	**Status under Reg. (EC) No 1107/2009 [b,c]**	**Date of approval[c]**	**Expiration of approval[c]**	**Priority substances to be monitored in the air in France (Hulin et al.,2021)**
Aclonifen	74070-46-5	Diphenyl ether	H	Y	01/08/2009	31/10/2026	
Chlorpropham	101-21-3	Carbamate	H	N	01/02/2005	08/07/2019	Yes
Clomazone	81777-89-1	Isoxazolidinone	H	Y	01/11/2008	15/06/2025	Yes
Diclofop-methyl	51338-27-3	Aryloxyphenoxypropionate	H	Y	01/06/2011	31/08/2026	
Diflufenican	83164-33-4	Carboxamide	H	Y	01/01/2009	15/01/2026	Yes
Dimethenamid-P	163515-14-8	Chloroacetamide	H	Y	01/09/2019	31/08/2034	Yes
Flazasulfuron	104040-78-0	Sulfonylurea	H	Y	01/08/2017	31/07/2032	
Flumioxazin	103361-09-7	N-phenylphtalamides	H	Y	01/01/2003	28/02/2037	
Flurochloridone	61213-25-0	Pyrrolidine	H	Y	01/06/2011	15/03/2026	
Isoproturon	34123-59-6	Urea	H	N	01/01/2003	30/06/2016	
Lenacil	01/08/2164	Uracil	H	Y	01/01/2009	15/08/2025	Yes
Linuron	330-55-2	Urea	H	N	01/01/2004	03/03/2017	Yes
Metazachlor	67129-08-2	Chloroacetamide	H	Y	01/08/2009	31/10/2026	Yes
Oxadiazon	19666-30-9	Oxidiazole	H	N	01/01/2009	31/12/2018	Yes
Pendimethalin	40487-42-1	Dinitroaniline	H	Y	01/01/2004	30/11/2024	Yes
Propyzamide	23950-58-5	Benzamide	H	Y	01/04/2004	30/06/2025	Yes
Prosulfocarb	52888-80-9	Thiocarbamate	H	Y	01/11/2009	31/01/2027	Yes
S-Metolachlor	87392-12-9	Chloroacetamide	H	Y	01/04/2005	15/11/2024	Yes
Terbuthylazine	5915-41-3	Triazine	H	Y	01/01/2012	31/12/2024	
Triallate	2303-17-5	Thiocarbamate	H	Y	01/01/2010	31/12/2022	Yes

Boscalid	188425-85-6	Carboxamide	F	Y	01/08/2008	15/04/2026	Yes
Cyprodinil	121552-61-2	Anilinopyrimidine	F	Y	01/05/2007	15/03/2025	Yes
Difenoconazole	119446-68-3	Triazole	F	Y	01/01/2009	15/03/2026	Yes
Dimethomorph	110488-70-5	Morpholine	F	Y	01/10/2007	15/02/2025	
Epoxiconazole	133855-98-8	Triazole	F	N	01/05/2009	30/04/2020	Yes
Fenhexamid	126833-17-8	Hydroxyanilide	F	Y	01/06/2001	31/12/2030	
Fenpropimorph	67564-91-4	Morpholine	F	N	01/05/2009	30/04/2019	
Fluazinam	79622-59-6	Phenylpyridinamine	F	Y	01/03/2009	15/04/2026	Yes
Flusilazole	85509-19-9	Triazole	F	N		30/06/2008	
Folpet	133-07-3	Dicarboximide	F	Y	01/10/2007	15/02/2025	Yes
Iprodione	36734-19-7	Imidazolidine	F	N	01/01/2004	05/12/2017	Yes
Kresoxim-methyl	143390-89-0	Strobilurin	F	Y	01/01/2012	31/12/2024	
Pyrimethanil	53112-28-0	Anilinopyrimidine	F	Y	01/06/2007	15/03/2025	Yes
Spiroxamine	118134-30-8	Morpholine	F	Y	01/01/2012	31/05/2026	Yes
Tebuconazole	107534-96-3	Triazole	F	Y	01/09/2009	15/08/2026	Yes
Tetraconazole	112281-77-3	Triazole	F	Y	01/01/2010	31/03/2027	
Tolylfluanid	731-27-1	Sulfamide	F	N		13/06/2011	Yes
Chlorpyrifos	2921-88-2	Organophosphate	I	N	01/07/2006	16/01/2020	Yes
Chlorpyrifos-methyl	5598-13-0	Organophosphate	I	N	01/07/2006	16/01/2020	Yes
Cypermethrin	52315-07-8	Pyrethroid	I	Y	01/03/2006	31/01/2029	Yes
Deltamethrin	52918-63-5	Pyrethroid	I	Y	01/11/2003	15/08/2026	Yes
Fenoxycarb	72490-01-8	Carbamate	I	N	01/06/2011	31/05/2021	
Fipronil	120068-37-3	Phenylpyrazole	I	N	01/10/2007	30/09/2017	Yes
Lambda-cyhalothrine	68085-85-8	Pyrethroid	I	Y	01/01/2002	31/08/2026	Yes
Lindane	58-89-9	Organochlorine	I	N		01/06/2002	Yes
Permethrin	52645-53-1	Pyrethroid	I	N		01/07/2002	Yes
Piperonyl butoxide	51-03-6	Heterocyclic	I synergist	Not yet assessed at EU level			Yes
Pirimicarb	23103-98-2	Carbamate	I	Y	01/02/2007	15/03/2025	Yes

[a] H: Herbicide, F: Fungicide, I: Insecticide

[b]: Y: Approved, N: Not approved

[c]: EU Pesticides Database - Active substances, (available at https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/start/screen/active-substances)

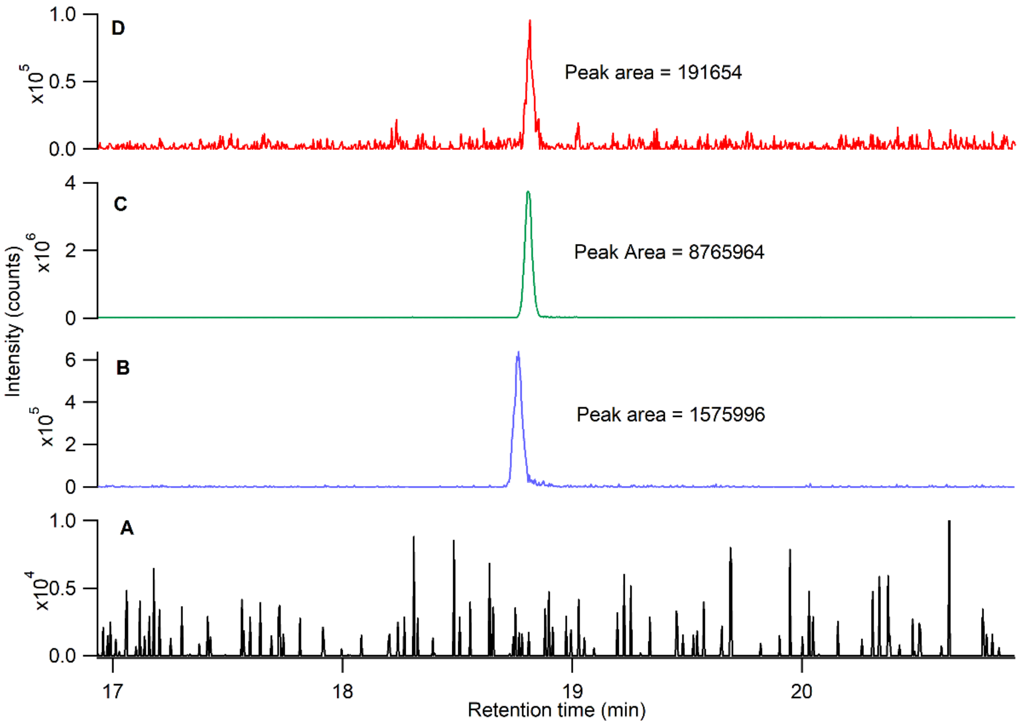
Table S2. Parameters of the Gas Chromatography – Mass Spectrometry tandem (GC-MS/MS) analysis in multi reaction monitoring (MRM) mode for the targeted pesticides with the transition used for quantification purposes (Q), qualifier transitions used for improving pesticide identification (q1, q2), and retention time (RT).

Pesticide	**Quantifier transition Q**	**Qualifier transition q1**	**Qualifier transition q2**	**RT (min)**
Aclonifen	264 --> 194	212 --> 182		17.9
Chlorpropham	213 --> 127	127 --> 65		10.0
Clomazone	125 --> 89	125 -->90	205 --> 107	10.0
Diclofop-methyl	253 --> 162	340 --> 253		19.6
Diflufenican	394 --> 266	266 --> 246		18.9
Dimethenamid-P	230 --> 154	153 --> 137	154 --> 121	12.2
Flazasulfuron	155 --> 154	154 -->126	155 --> 57	7.7
Flumioxazin	354 --> 176	287 --> 259	354 --> 312	27.3
Flurochloridone	311 --> 174	311 --> 187	187 --> 109	14.0
Isoproturon	161 --> 146	128 --> 101		7.1
Lenacil	153 --> 136	153 --> 135	154 --> 136	18.9
Linuron	248 --> 61	160 --> 133	160 --> 125	13.3
Metazachlor	209 --> 132	209 --> 133	209 --> 117	14.5
Oxadiazon	258 --> 175	304 -->260		16.5
Pendimethalin	252 --> 162	252 --> 191		14.4
Propyzamide	254 --> 226	145 --> 109	173 --> 109	11.2
Prosulfocarb	251 --> 128	251 --> 218		13.0
S-metolachlor	238 -->162	238 --> 133	162 --> 133	13.5
Terbuthylazine	214 --> 132	229 --> 214	229 --> 173	11.1
Triallate	268 --> 184	268 --> 226	270 --> 186	11.7
Boscalid	342 --> 140	344 --> 142		25.7
Cyprodinil	225 --> 210	225 --> 132		14.4
Difenoconazole	323 --> 265	325 --> 267		28.2
Dimethomorph	301 --> 165	387 --> 301	301 -- > 165	29.4
Epoxiconazole	192 --> 138	192 --> 111	192 --> 102	19.9
Fenhexamid	177 --> 113	301 --> 97		19.0
Fenpropimorph	303 --> 128	128 -->110	128 --> 70	13.7
Fluazinam	418 --> 372	417 --> 388		14.3
Flusilazole	233 --> 183	233 --> 152	233 --> 165	16.6
Folpet	260 --> 130	260 --> 233	260 --> 95	15.1
Iprodione	314 --> 245	187 --> 124		20.4
Kresoxym-methyl	206 --> 131	206 --> 116		16.8
Pyrimethanil	198 --> 118	198 --> 158	199 --> 198	11.4
Spiroxamine	100 --> 72	100 --> 58		11.9
Tebuconazole	250 --> 125	252 --> 127		19.5
Tetraconazole	336 --> 204	336 --> 218	338 --> 220	13.8
Tolylfluanid	238 --> 137	181 --> 138		14.7
Chlorpyrifos	314 --> 258	314 --> 286	197 --> 169	13.5
Chlorpyrifos-methyl	286 --> 272	286 --> 208	286 --> 93	12.4
Cypermethrin	163 --> 127	181 --> 152		25.7

Deltamethrin	253 --> 174	251 --> 172		28.1
Fenoxycarb	186 --> 109	255 --> 186		20.9
Fipronil	367 --> 213	367 --> 255	370 --> 215	14.6
Lambda-cyhalothrin	197 --> 141	208 --> 181	181 --> 152	22.6
Lindane	181 --> 145	219 --> 181	183 --> 147	11.1
Permethrin	183 --> 165	183 --> 168		24.0
Piperonyl butoxide	176 --> 117	338 --> 176	176 --> 131	19.8
Pirimicarb	238 --> 166	166 --> 96	166 --> 137	11.7

Fig.S1. Example of extracted ion chromatograms for a) the MRM transitions 394->266 (quantifier transition Q) and b) 266->246 (qualifier transition q1) of an analytical blank (A), a diflufenican standard solution 0.01 mg.L^{-1} (B), lichen sample CAB (C) and lichen sample FOA (D). Diflufenican was identified with the correspondence of the retention time (RT=18,9 min) and the peak area ratios between transitions (area ratio Q/q1 = 1.1)

a) MRM transition 394->266



b) MRM transition 266->246

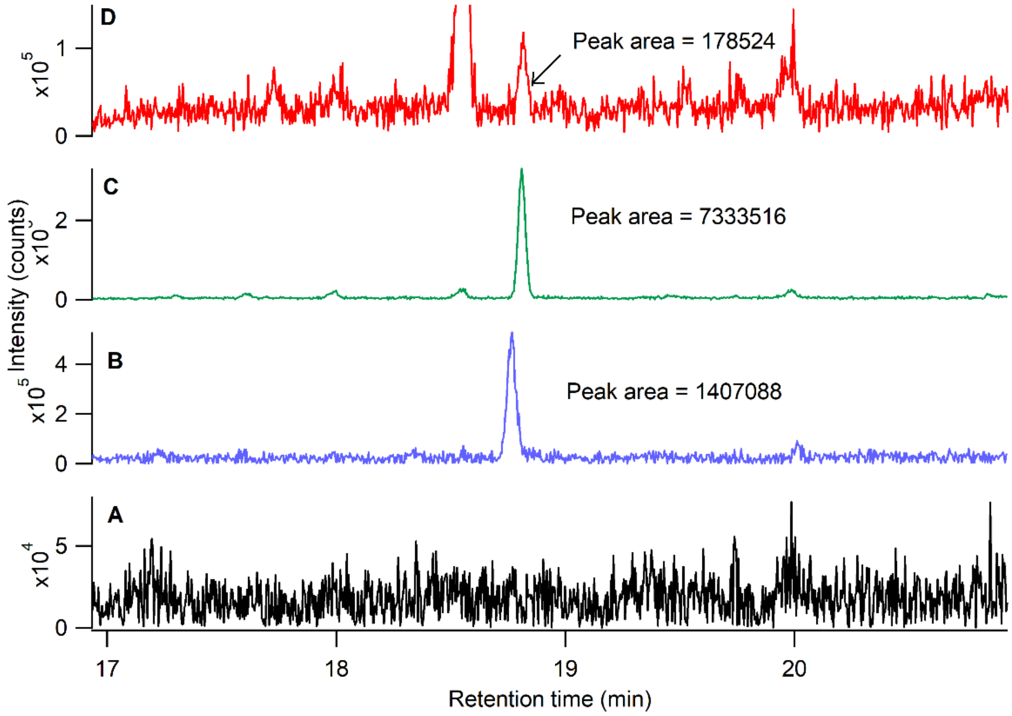


Table S3. Mean % of recoveries (3 replicates) obtained with different combinations of extraction solvent and clean-up sorbent on a lichen matrix spiked with pesticides. At this step, concentrations were not corrected by the internal standard. DCM: dichloromethane, ACN: acetonitrile.

Extraction solvent	**DCM**	**DCM**	**DCM**	**ACN**	**ACN**	**ACN**
Clean-up sorbent	**Oasis HLB**	**Florisil**	**EnviCarb/ PSA**	**Oasis HLB**	**Florisil**	**EnviCarb/PSA**
Aclonifen	31	50	100	91	21	0
Chlorpropham	132	163	127	130	51	59
Clomazone	105	137	66	114	37	58
Diclofop-methyl	103	129	53	79	29	11
Diflufenican	73	128	41	73	21	23
Dimethenamid-P	120	159	58	95	34	62
Flazasulfuron	0	0	42	91	27	51
Flumioxazin	513	646	10	148	28	0
Flurochloridone	99	140	42	79	26	68
Isoproturon	48	90	40	49	28	37
Lenacil	390	473	43	106	30	91
Linuron	75	138	42	78	30	0
Metazachlor	107	143	46	78	12	63
Oxadiazon	94	124	37	78	26	58
Pendimethalin	185	239	49	94	36	0
Propyzamide	117	147	39	97	28	57
Prosulfocarb	109	146	37	93	27	53

S-metolachlor	114	139	36	81	25	62
Terbuthylazine	113	238	49	143	36	41
Triallate	108	137	38	95	26	49
Boscalid	173	207	0	117	23	0
Cyprodinil	105	150	39	86	30	0
Difenoconazole	347	365	0	167	28	0
Dimethomorph	572	322	38	208	28	0
Epoxiconazole	116	151	35	89	29	0
Fenhexamid	778	369	28	103	16	0
Fenpropimorph	101	133	57	73	36	46
Fluazinam	0	0	31	21	22	57
Flusilazole	127	160	59	82	39	107
Folpet	0	0	38	22	28	58
Iprodione	267	341	48	93	37	66
Kresoxym-methyl	126	154	51	75	42	68
Pyrimethanil	106	136	16	86	35	4
Spiroxamine	106	19	34	111	24	48
Tebuconazole	106	131	62	86	46	37
Tetraconazole	105	132	16	88	28	49
Tolylfluanid	0	0	40	27	30	90
Chlorpyrifos	114	143	51	85	35	0
Chlorpyrifos-methyl	115	159	38	77	29	0
Cypermethrin	244	301	37	122	26	0
Deltamethrin	277	464	38	105	28	0
Fenoxycarb	99	113	39	89	28	61
Fipronil	164	267	43	67	34	0
Lambda-cyhalothrin	172	225	40	93	31	65
Lindane	70	101	41	82	38	40
Permethrin	148	174	105	92	75	21
Piperonyl butoxyde	139	170	37	83	33	0
Pirimicarb	113	144	65	93	46	16
TPP (Internal standard)	114	132	71	84	42	0

Table S4. Pesticides concentrations in µg.kg^{-1} in lichens sampled on urban (U) sites. For details of site names, see table 1.

	AIX	CHF	MN1	MN2	MRS	MS1	MS2	MS3	SME	SMN	SMO
Aclonifen	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpropham	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Clomazone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diclofop-methyl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diflufenican	**0.9**	**1.9**	**0.5**	**1.5**	**0.6**	**<LOQ**	**<LOQ**	**<LOQ**	**0.6**	**<LOQ**	**1.2**
Dimethenamid-P	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flazasulfuron	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flumioxazin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flurochloridone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Isoproturon	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lenacil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Linuron	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Metazachlor	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oxadiazon	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pendimethalin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propyzamide	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Prosulfocarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S-metolachlor	<LOD	<LOD	<LOD	<LOD	<LOD	**<LOQ**	<LOD	**<LOQ**	<LOD	<LOD	<LOD
Terbuthylazine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Triallate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Boscalid	**<LOQ**	**4.1**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**0.9**
Cyprodinil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Difenoconazole	**7.5**	**16.9**	**2.2**	**1.6**	**2.7**	**<LOQ**	**<LOQ**	**<LOQ**	**2.5**	**<LOQ**	**4.2**
Dimethomorph	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Epoxiconazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fenhexamid	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fenpropimorph	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fluazinam	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flusilazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Folpet	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Iprodione	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Kresoxym methyl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pyrimethanil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**<LOQ**	<LOD	**<LOQ**	<LOD	**<LOQ**
Spiroxamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tebuconazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**<LOQ**	<LOD	**5.8**
Tetraconazole	<LOD	<LOD	<LOD	<LOD	**<LOQ**	<LOD	<LOD	<LOD	**<LOQ**	<LOD	**<LOQ**
Tolylfluanid	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpyrifos	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpyrifos_m	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

ethyl											
Cypermethrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Deltamethrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fenoxycarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fipronil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lambda cyhalothrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lindane	**<LOQ**	**3.7**	**1.3**	**LOQ**	**1.7**	**LOQ**	**1.5**	**1.1**	**1.2**	**2.5**	**1.2**
Permethrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Piperonyl butoxyde	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pirimicarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Total	8.4	26.6	4.0	3.1	5.1	<LOQ	1.5	1.1	4.3	2.5	13.3

Table S5. Pesticides concentrations in µg.kg^{-1} in lichens sampled on urban/industrial (UI) sites. For details of site names, see table 1.

	ENG	FOA	FOM	GAR	PSL-S3	PSL-S10
Aclonifen	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpropham	<LOD	<LOD	<LOD	<LOD	**<LOQ**	<LOD
Clomazone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diclofop-methyl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diflufenican	**<LOQ**	**2.1**	**2.3**	**0.9**	**2.4**	**3.3**
Dimethenamid-P	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flazasulfuron	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flumioxazin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Flurochloridone	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Isoproturon	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lenacil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Linuron	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Metazachlor	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Oxadiazon	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pendimethalin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propyzamide	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Prosulfocarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S-metolachlor	<LOD	<LOD	<LOD	<LOD	<LOD	**8.0**
Terbuthylazine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Triallate	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Boscalid	**<LOQ**	**1.3**	**<LOQ**	**<LOQ**	**5.3**	**3.1**
Cyprodinil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Difenoconazole	**<LOQ**	**2.2**	**<LOQ**	**<LOQ**	**79.4**	**24.5**
Dimethomorph	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Epoxiconazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fenhexamid	<LOD	<LOD	<LOD	<LOD	**37.9**	<LOD
Fenpropimorph	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fluazinam	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Flusilazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Folpet	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Iprodione	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Kresoxym methyl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pyrimethanil	**<LOQ**	**<LOQ**	**<LOQ**	<LOD	<LOD	<LOD
Spiroxamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tebuconazole	<LOD	<LOD	<LOD	<LOD	**35.3**	**11.1**
Tetraconazole	<LOD	<LOD	**<LOQ**	<LOD	<LOD	<LOD
Tolylfluanid	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpyrifos	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Chlorpyrifos_methyl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cypermethrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Deltamethrin	<LOD	<LOD	<LOD	<LOD	<LOD	**13.4**
Fenoxycarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fipronil	<LOD	<LOD	<LOD	<LOD	**3.6**	<LOD
Lambda cyhalothrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lindane	**1.2**	**2.1**	**4.0**	**<LOQ**	**4.5**	**3.3**
Permethrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Piperonyl butoxyde	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Pirimicarb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Total	1.2	7.7	6.3	0.9	168.4	66.8

Table S6. Pesticides concentrations in µg.kg^{-1} in lichens sampled on industrial (I) sites. For details of site names, see table 1.

	CAB	GOU	TON
Aclonifen	<LOD	<LOD	<LOD
Chlorpropham	<LOD	<LOD	<LOD
Clomazone	<LOD	<LOD	<LOD
Diclofop-methyl	<LOD	<LOD	<LOD
Diflufenican	**64.8**	**1.7**	**<LOQ**
Dimethenamid-P	<LOD	<LOD	<LOD
Flazasulfuron	<LOD	<LOD	<LOD
Flumioxazin	<LOD	<LOD	<LOD
Flurochloridone	<LOD	<LOD	<LOD
Isoproturon	<LOD	<LOD	<LOD
Lenacil	<LOD	<LOD	<LOD
Linuron	<LOD	<LOD	<LOD
Metazachlor	<LOD	<LOD	<LOD
Oxadiazon	<LOD	<LOD	<LOD
Pendimethalin	**19.6**	<LOD	<LOD
Propyzamide	<LOD	<LOD	<LOD
Prosulfocarb	<LOD	<LOD	<LOD
S-metolachlor	**<LOQ**	**<LOQ**	<LOD
Terbuthylazine	<LOD	<LOD	<LOD
Triallate	<LOD	<LOD	<LOD

Boscalid	**1.6**	**1.8**	**<LOQ**
Cyprodinil	<LOD	<LOD	<LOD
Difenoconazole	**3.6**	**2.8**	**<LOQ**
Dimethomorph	<LOD	<LOD	<LOD
Epoxiconazole	<LOD	<LOD	<LOD
Fenhexamid	<LOD	<LOD	<LOD
Fenpropimorph	<LOD	<LOD	<LOD
Fluazinam	<LOD	<LOD	<LOD
Flusilazole	<LOD	<LOD	<LOD
Folpet	<LOD	<LOD	<LOD
Iprodione	<LOD	<LOD	<LOD
Kresoxym methyl	<LOD	<LOD	<LOD
Pyrimethanil	**<LOQ**	**<LOQ**	**<LOQ**
Spiroxamine	<LOD	<LOD	<LOD
Tebuconazole	<LOD	<LOD	<LOD
Tetraconazole	**<LOQ**	**0.9**	<LOD
Tolylfluanid	<LOD	<LOD	<LOD
Chlorpyrifos	**1.8**	**1.2**	<LOD
Chlorpyrifos_methyl	<LOD	<LOD	<LOD
Cypermethrin	**8.0**	**12.4**	<LOD
Deltamethrin	**<LOQ**	**11.7**	<LOD
Fenoxycarb	<LOD	<LOD	<LOD
Fipronil	<LOD	<LOD	<LOD
Lambda cyhalothrin	<LOD	<LOD	<LOD
Lindane	**1.9**	**2.2**	**2.2**
Permethrin	<LOD	<LOD	<LOD
Piperonyl butoxyde	<LOD	<LOD	<LOD
Pirimicarb	<LOD	<LOD	<LOD
Total	101.3	34.7	2.2

Table S7. Pesticides concentrations in µg.kg^{-1} in lichens sampled on rural (R) sites. For details of site names, see table 1.

	COR	CPH	ENT	TNT
Aclonifen	<LOD	<LOD	<LOD	<LOD
Chlorpropham	<LOD	<LOD	<LOD	<LOD
Clomazone	<LOD	<LOD	<LOD	<LOD
Diclofop-methyl	<LOD	<LOD	<LOD	<LOD
Diflufenican	**2.1**	**0.6**	**1.2**	**1.2**
Dimethenamid-P	<LOD	<LOD	<LOD	<LOD
Flazasulfuron	<LOD	<LOD	<LOD	<LOD
Flumioxazin	<LOD	<LOD	<LOD	<LOD
Flurochloridone	<LOD	<LOD	<LOD	<LOD
Isoproturon	<LOD	<LOD	<LOD	<LOD
Lenacil	<LOD	<LOD	<LOD	<LOD
Linuron	<LOD	<LOD	<LOD	<LOD
Metazachlor	<LOD	<LOD	<LOD	<LOD
Oxadiazon	<LOD	<LOD	<LOD	<LOD
Pendimethalin	<LOD	<LOD	<LOD	<LOD
Propyzamide	<LOD	<LOD	<LOD	<LOD

Prosulfocarb	<LOD	<LOD	<LOD	<LOD
S-metolachlor	<LOD	<LOD	<LOD	<LOD
Terbuthylazine	<LOD	<LOD	<LOD	<LOD
Triallate	<LOD	<LOD	<LOD	<LOD
Boscalid	**5.2**	**<LOQ**	**3.0**	**<LOQ**
Cyprodinil	<LOD	<LOD	<LOD	<LOD
Difenoconazole	**23.1**	**1.4**	**4.7**	**2.4**
Dimethomorph	<LOD	<LOD	<LOD	<LOD
Epoxiconazole	<LOD	<LOD	<LOD	<LOD
Fenhexamid	<LOD	<LOD	<LOD	<LOD
Fenpropimorph	<LOD	<LOD	<LOD	<LOD
Fluazinam	<LOD	<LOD	<LOD	<LOD
Flusilazole	<LOD	<LOD	<LOD	<LOD
Folpet	<LOD	<LOD	<LOD	<LOD
Iprodione	<LOD	<LOD	<LOD	<LOD
Kresoxym methyl	<LOD	<LOD	<LOD	<LOD
Pyrimethanil	<LOD	**<LOQ**	**<LOQ**	<LOD
Spiroxamine	<LOD	<LOD	<LOD	<LOD
Tebuconazole	<LOD	<LOD	<LOD	<LOD
Tetraconazole	<LOD	**<LOQ**	**<LOQ**	<LOD
Tolylfluanid	<LOD	<LOD	<LOD	<LOD
Chlorpyrifos	<LOD	<LOD	**1.1**	<LOD
Chlorpyrifos_methyl	<LOD	<LOD	<LOD	<LOD
Cypermethrin	<LOD	<LOD	**24.6**	<LOD
Deltamethrin	<LOD	<LOD	**25.1**	<LOD
Fenoxycarb	<LOD	<LOD	<LOD	<LOD
Fipronil	<LOD	<LOD	<LOD	<LOD
Lambda cyhalothrin	<LOD	<LOD	<LOD	<LOD
Lindane	**3.8**	**1.2**	**2.6**	**1.2**
Permethrin	<LOD	<LOD	<LOD	<LOD
Piperonyl butoxyde	<LOD	<LOD	<LOD	<LOD
Pirimicarb	<LOD	<LOD	<LOD	<LOD
Total	34.2	3.2	62.3	4.8

References

Hulin, M., Leroux, C., Mathieu, A., Gouzy, A., Berthet, A., et al., 2021. Monitoring of pesticides in ambient air: Prioritization of substances. Sci. Total Environ. 753, 141722. https://doi.org/10.1016/j.scitotenv.2020.141722.